# Argon Plasma Treatment of Packing Materials for Gas Chromatography and Comparison with Acid Wash and Dimethyldichlorosilane Treatment of Support

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Argon plasma treatment of column packings for gas chromatography was examined with commercially obtained diatomaceous earth coated with several kinds of stationary liquid phases, such as squalane, Apiezon L, dioctyl phthalate, Silicone DC, and polyethylene glycol. It was found that the plasma treatment improves chromatographic properties of all the packings examined except those with polyethylene glycol. The effect of the plasma treatment is attributable to the reduction of support adsorptivity by the formation of an inert coating on the support surface. The plasma treatment of Chromosorb W coated with 5% squalane was compared with dimethyldichlorosilane (DMCS) treatment of the acid-washed (AW) support, the so-called AW-DMCS-treatment of support. Although the AW-DMCS-treatment is superior to the plasma treatment for the reduction of support adsorptivity, a complete elimination of the adsorptivity was attained by the plasma treatment of the packing having the AW-DMCS-treated support.

Preceding papers have illustrated the effect of argon plasma treatment of diatomaceous earth coated with squalane or Apiezon L on gas chromatograms of hydrocarbons.[1,2] By the plasma treatment, the chromatographic resolution was improved and the retention times were decreased. The effect has been attributed to the reduction of support adsorptivity by the formation of an inert coating on the support surface, based on the following results. (1) By the plasma treatment, the tailings of aromatic hydrocarbon peaks were reduced, and their retention times were decreased more than those of saturated aliphatic hydrocarbons. (2) The weight loss of the packing treated which occurred by the extracting the stationary liquid phase decreased with increasing treatment time, indicating the formation of an insoluble component on the support surface. (3) The ESCA spectrum of the support recovered from the treated packing by extracting the liquid phase indicated that the support surface is covered with an organic component. (4) NMR spectrometry showed that the soluble fraction of liquid phase of the treated packing remains unchanged.

The experiments described here were undertaken to enhance the utility of argon plasma treatment for the improvement of chromatographic properties of column packings. The plasma treatment of various kinds of familiar packings was examined. A comparison was made with dimethyldichlorosilane (DMCS) treatment of acid-washed (AW) support, the so-called AW-DMCS-treatment of support, which is usually used to reduce the support adsorptivity.

## Experimental

Column packings (60/80 mesh) were obtained from Wako Pure Chemical Industry. The apparatus and experimental details of the plasma treatment were described previously.[2] The gas chromatographic test of the treated packing was also carried out as described previously; the packing was packed into a 1 m×3 mm i.d. stainless steel tube, and the nitrogen flow rate was 30 ml/min. Before its use, the packing was conditioned longer than overnight at a temperature 10 °C below the maximum temperature of the packing.

## Results and Discussion

Figure 1 shows the effect of argon plasma treatment of Chromosorb W (non-acid washed (NAW)) coated with 5% squalane (max. temp, 140 °C) on the gas chromatogram of aromatic ketones. The retention times and tailings of the peaks are reduced by the plasma treatment. On the 60 min treated packing, sharp peaks with improved separations are obtained. A similar effect was also observed on the gas chromatogram of aliphatic ketones such as 5-nonanone and 6-undecanone. The results suggest that the plasma treatment enables the packing to be used for the

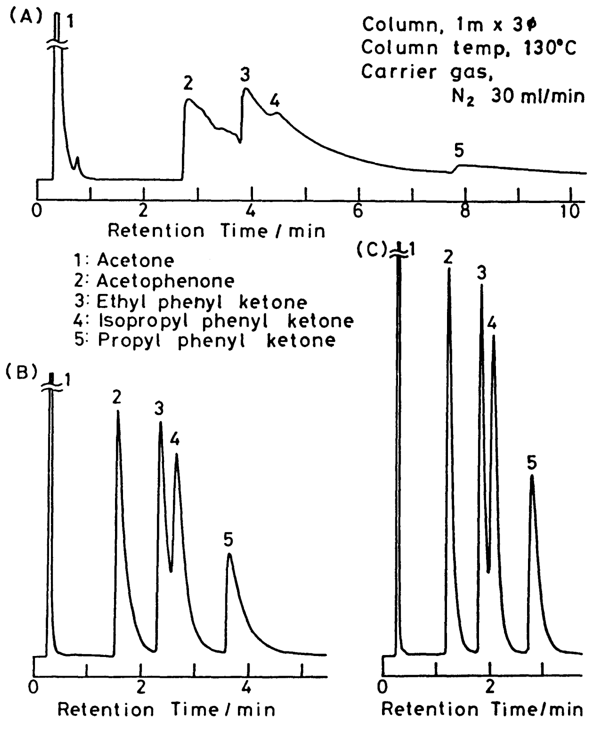


Fig. 1. Gas chromatograms on Chromosorb W (NAW) coated with 5% squalane: (A) untreated; (B) 30 min plasma treated; (C) 60 min plasma treated.

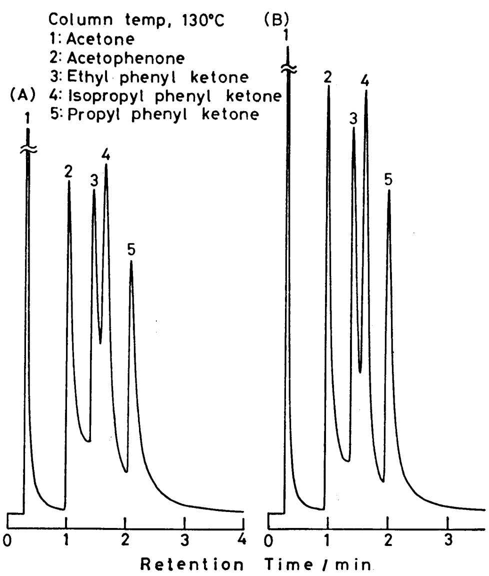


Fig. 2. Gas chromatograms on Chromosorb W (NAW) coated with 5% Silicone DC 200: (A) untreated; (B) 60 min plasma treated.

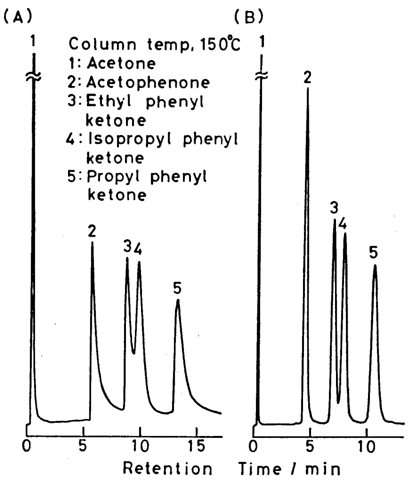


Fig. 3. Gas chromatograms on Shimalite (NAW) coated with 25% Silicone DC 702: (A) untreated; (B) 90 min plasma treated.

analysis of ketones as well as hydrocarbons.

Figures 2 and 3 show the gas chromatograms of the aromatic ketones on untreated and treated packings, Chromosorb W (NAW) coated with 5% Silicone DC 200 (max. temp, 200 °C) and Shimalite (NAW) coated with 25% Silicone DC 702 (max. temp, 200 °C), respectively. The decrease in the retention times and the improvement of peak separations by the plasma treatment are also observed with these packings.

Similar results were obtained by the plasma treatment of other kinds of packings: Chromosorb W (NAW) coated with 20% Apiezon L and 10% KOH (max. temp, 180 °C) and Chromosorb W (NAW) coated with 10% dioctyl phthalate (max. temp, 140 °C). The former packing is used for the analysis of amines, and the latter for the analysis of alcohols and esters. Examples of the gas chromatograms on these packings are shown in Figs. 4 and 5, illustrating

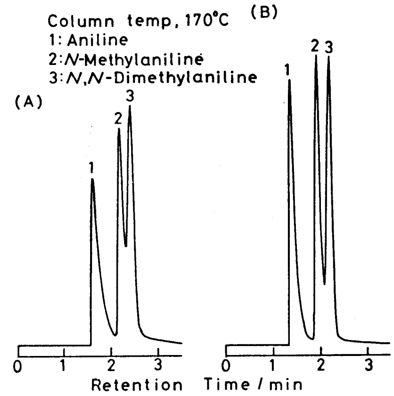


Fig. 4. Gas chromatograms on Chromosorb W (NAW) coated with 20% Apiezon L and 10% KOH: (A) untreated; (B) 10 min plasma treated.

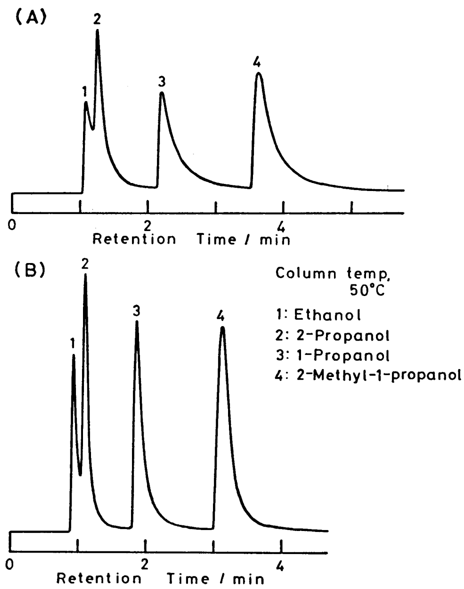


Fig. 5. Gas chromatograms on Chromosorb W (NAW) coated with 10% dioctyl phthalate: (A) untreated; (B) 60 min plasma treated.

the improvement of their chromatographic properties by the plasma treatment.

By the plasma treatment the retention times and tailings of chromatographic peaks were reduced in all the cases of the packings described above, although the treatment times needed for an appreciable effect to occur on the gas chromatograms differ from one another. The prolonged plasma treatment resulted in further decrease in the retention times accompanying a decrease in the peak separations. According to the previous studies,[1,2] it is reasonable to assume that the effect of the plasma treatment of these packings is due to the reduction of support adsorptivity.

The surface of the diatomite supports is covered with reactive silanol groups, which cause tailings of chromatographic peaks,[3] and the AW-DMCS-treated supports are usually used to avoid the adsorption on the support surface. Thus, it is interesting to compare the effect of the plasma treatment of packing with that of the AW-DMCS-treatment of support,

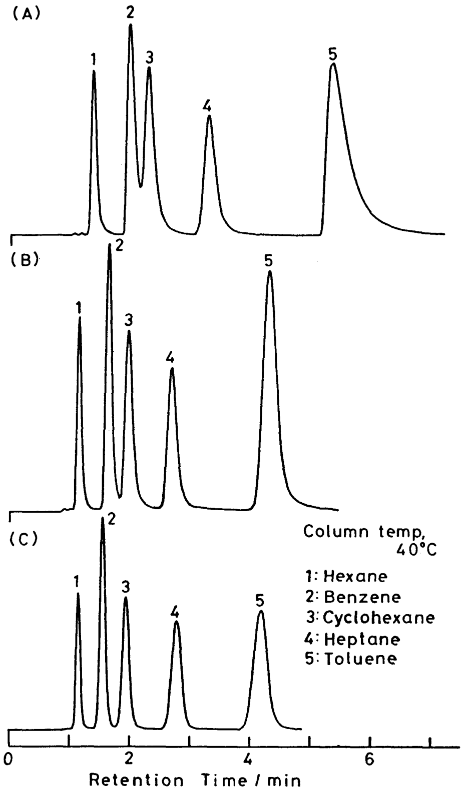


Fig. 6. Gas chromatograms on Chromosorb W coated with 5% squalane: (A) untreated packing, AW support; (B) 30 min plasma treated packing, AW support; (C) untreated packing, AW-DMCS treated support.

Figure 6 illustrates the gas chromatograms of a hydrocarbon mixture on Chromosorb W (NAW) coated with 5% squalane, in order to compare the effect of the plasma treatment of the packing having the AW support with that of the AW-DMCS-treatment. These chromatograms should also be compared with those on the untreated and treated packings having the NAW support, which have previously been shown in Ref. 1 (Fig. 3). A comparison of the figures shows that the chromatograms on the 30 min plasma treated packings having the NAW and AW supports (Fig. 3(b) in Ref. 1 and Fig. 6(B), respectively) are almost identical with that on the untreated packing having the AW-DMCS-treated support (Fig. 6(C)). On these packings, benzene and cyclohexane are well separated and the tailing of the peak of toluene is completely suppressed in contrast to the untreated packings having the NAW and AW supports (Fig. 3(a) in Ref. 1 and Fig. 6(A), respectively). That is to say, the effect of the plasma treatment of the packings having the NAW and AW supports on the gas chromatograms of the hydrocarbon mixture is almost the same as that of the AW-DMCS-treatment of support. It is also shown that, on the untreated packings, the AW support is better for the separation of benzene and cyclohexane than the NAW support (Fig. 6(A) compared with Fig. 3(a) in Ref. 1).

Since polar compounds are sensitive to the support adsorptivity and are expected to give more detailed information about it than the hydrocarbons, the gas chromatograms of alcohols on the packings with 5% squalane are compared in Fig. 7. On the 60 min treated packing having the NAW support, the peaks are very broad with extensive tailings. The tailings are appreciably reduced on the untreated packing having the AW-DMCS-treated support, indicating that the AW-DMCS-treatment of support is superior to the plasma treatment of the packing for the reduction of the support adsorptivity. However, a complete suppression of the tailings is attained by the 30 min plasma treatment of the packing having the AW-DMCS treated support, as is shown by Fig. 7(C). Thus, the plasma treatment is useful for the complete suppression of the adsorption on the support surface when used together with the AW-DMCS-treatment of support.

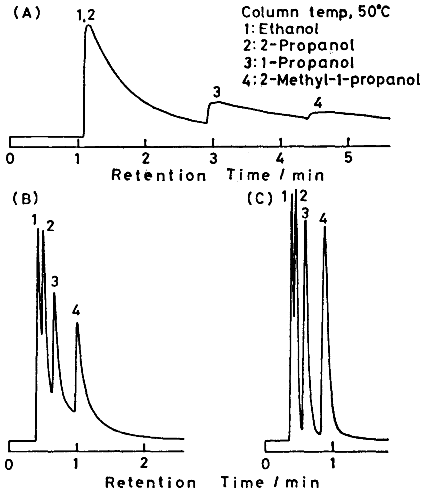


Fig. 7. Gas chromatograms on Chromosorb W coated with 5% squalane: (A) 60 min plasma treated packing, NAW support; (B) untreated packing, AW-DMCS treated support; (C) 30 min plasma treated packing, AW-DMCS treated support.

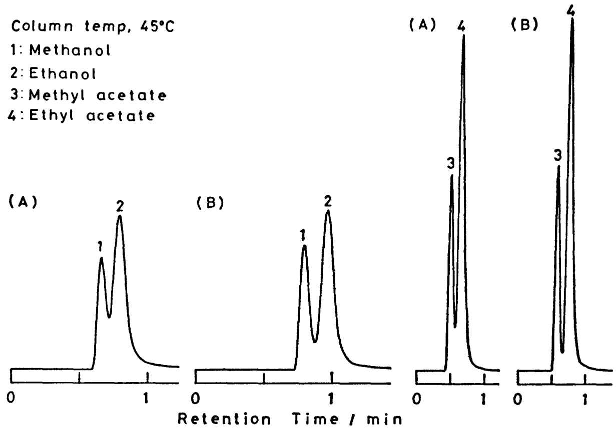


Fig. 8. Gas chromatograms on Chromosorb W (NAW) coated with 10% polyethylene glycol 20M: (A) untreated; (B) 20 min plasma treated.

The effect of the plasma treatment of diatomaceous earth coated with polyethylene glycol was different from that of the other packings described above; the plasma treatment tends to increase the retention times on the packings. Figure 8 shows the gas chromatograms of alcohols and esters on the untreated and treated Chromosorb W (NAW) coated with 10% polyethylene glycol 20 M (max. temp, 200 °C), demonstrating that both the retention times and the peak separations are increased by the plasma treatment. The plasma treatment of Shimalite (base-treated) coated with 25% polyethylene glycol 6000 (max. temp, 200 °C) was also examined, but the observed effect on the gas chromatograms was only a slight increase in the retention times. Such exceptional results can be ascribed to the high polarity of the liquid phase; the adsorption on support surface is not important on the packings with the polar liquid phase. In practice, tailings of the peaks are not observed even on the untreated packings. The increase in the retention times by the plasma treatment is probably due to some modification of the liquid phase.

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### References

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